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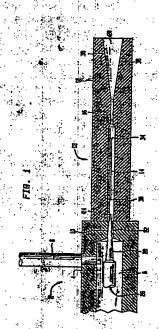
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Apparatus and method for removing minute particles from a substrate.

Apparatus for removing small particles from a substrate comprises a source of fluid carbon dioxide, a first orifice (10) for expanding a portion of the fluid carbon dioxide and find droplets of liquid carbon dioxide, a coalescing chamber (14) for converting the first mixture into a second mixture containing gaseous carbon dioxide and larger liquid droplets of carbon dioxide, a second expansion orifice (16) for converting said second mixture into a third mixture containing solid particles of carbon dioxide and gaseous carbon dioxide, and a divergibilit channel 20 having an exit port arranged to direct mixture toward the substrate. In using the apparatus, a source of fluid carbon dioxide having an enthalpy below about 135 BTU per pound (based on an enthalpy of zero at 150 psia for a saturated liquid) is employed.



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## APPARATUS AND METHOD FOR REMOVING MINUTE PARTICLES FROM A SUBSTRATE

The present invention is directed to apparatus and methods for removing minute particles from a substrate employing a stream containing solid and gaseous carbon dioxide. The apparatus of the invention is especially suited for removing submicron contaminants from semi-conductor substrates.

The removal of finely particulate surface contamination has been the subject of numerous investigations, especially in the semi-conductor industry. Large particles, ie in excess of one micron, are easily removed by blowing with a dry nitrogen stream. However, submicron particles are more strongly bound to the substrate surface. This is due primarily to electrostatic forces and bonding of the particles by surface layers containing absrobed water and/or organic compounds. In addition, there is a boundary layer of nearly stagnant gas on the surface which is comparatively think in relation to submicron particles. This layer shields submicron particles from forces which moving gas streams would otherwise exert on them at greater distances from the surface.

It is generally believed that the high degree of adhesion of submicron particles to a substrate is due to the relatively large surface area of the particles which provides greater contact with the substrate. Since such particles do not extend far from the surface area and therefore have less surface area exposed to the stream of a gas or liquid, they are not easily removed by aerodynamic drag effects as evidenced by studies of the movement of sand and other small particles. Bagnold, R. The Physics of Sand and Desert Dunes, Chapman and Hall, London (1966); and Corn, M. "The Adhesion of Solid Particles to Solid Surfaces", J. Air. Poll. Cart. Assoc. Vol 11, No 11 (1961).

The semiconductor industry has employed high pressure liquids alone or in combination with fine bristled brushes to remove finely particulate contaminants from semiconductor wafers. While such processes have achieved some success in removing contaminants, they are disadvantageous because the brushes scratch the substrate surface and the high pressure liquids tend to erode the delicate surfaces and can even generate an undesirable electric discharge as noted by Gallo, C. F. and Lama, W.C. "Classical Electrostatic Description of the Work Function and Ionization Energy of Insulators", IEEE Trans. Ind. Appl. Vol 1A-12, No 2 (Jan/Feb 1976). Another disadvantage of the brush and high pressure liquid systems is that the liquids can not readily by collected after use.

In accordance with the present invention, a mixture of substantially pure solid and gaseous carbon dioxide has been found effective for removal of submicron particles from substrate surfaces without the disadvantages associated with the above-described brush and high pressure liquid systems.

More specifically, pure carbon dioxide (99.99 + %) is available and can be expanded from the liquid state to produce dry ice snow which van be effectively blown across a surface to remove sumicron particles without scratching the substrate surface. In addition, the carbon dioxide snow vaporizes when exposed to ambient temperatures leaving no residue and thereby eliminating the problem of fluid collection.

Ice and dry ice have been described as abrasive cleaners. For example, E J Courts, in US Patent No 2 699 403, discloses apparatus for producing ice flakes from water for cleaning the exterior surfaces of automobiles. U C Walt et al, in US Patent No 3 074 822, disclose apparatus for generating a fluidized frozen dioxane and dry ice mixture for cleaning surfaces such as gas turbine blades. Walt et al state that dioxane is added to the dry ice because the latter does not evidence good abrasive and solvent action.

More recently, apparatus for making carbon dioxide snow and for directing a solid/gas mixture of carbon dioxide to a substrate has been disclosed. Hoenig, Stuart A. "The Application of Dry Ice to the Removal of Particulates from Optical Apparatus, Spacecraft, Semiconductor Wafers, and Equipment Used in Contaminant Free Manufacturing Processes" (Compressed Air Magazine, August 1986, pp 22-25). By this device, liquid carbon dioxide is depressurized through a long, cylindrical tube of uniform diameter to produce a solid/gas carbon dioxide mixture which is then directed to the substrate surface. A concentrically positioned tube is used to add a flow of dry nitrogen gas to thereby prevent the build-up of condensation.

Despite being able to remove some submicron particles, the aforementioned device suffers from several disadvantages. For example, the cleaning effect is limited primarily due to the low gas velocity and the flaky and fluffy nature of the solid carbon dioxide. In addition, the geometry of the long cylindrical tube makes it difficult to control the carbon dioxide feed rate and the rate at which the snow stream contacts the substrate surface.

In accordance with this invention, there is provided a new apparatus for removing submicron particles from a substrate which overcomes the aforementioned disadvantages. The apparatus of this invention produces a solid/gas mixture of carbon dioxide at a controlled flow rate which effectively removes submicron particles from a substrate surface.

According to the present invention there is provided apparatus for removing small particles from a substrate comprising a source of fluid carbon dioxide under pressure and having an enthalpy of below about 135 BTU per pound based on an enthalpy of zero at 150 psia for a saturated liquid, so that a solid fraction will form upon expansion of the fluid carbon dioxide to the ambient pressure of said substrate; a first exapansion means for expanding a portion of the fluid carbon dioxide obtained from the source into a first mixture containing gaseous carbon dioxide and fine dropl ts of liquid carbon dioxide; a coalescing means operatively communicating with the first expansion means for converting said first mixture into a second mixture containing gaseous carbon dioxide and larger liquid droplets of carbon dioxid; a second expansion means operatively communicating with the coalescing means for converting said second mixture into a third mixture

containing solid particles of carbon dioxide and gaseous carbon dioxide; and means committicating with said second expansion means for directing said third mixture toward the substrate.

The Invention also provides a method for removing particles from a substrate surface, comprising converting fluid carbon dioxide into a first mixture of fine droplets of liquid carbon dioxide and gaseous carbon dloxid ; converting said first mixture into a second potential parties of liquid carbon dloxide and gaseous carbon dloxid; converting said second mixture lino a third mixture containing solid carrier dioxide particles and gaseous carbon dioxide; and directing said third mixture; toward the substrate whereby said third mixture removes said particles from the substrate.

The pr sent invention will now be described by way of example with refer not to accompanying drawings in

FIGURE 1 is a cross-sectional elevational view of the apparatus of the present invention employing a needle valve to control the rate of formation of fine droplets of carbon dioxide

FIGURE 2 is a cross-section elevational view of another embodiment of the invention which includes means for generating a dry nitrogen stream surrounding the solid/gaseous mixture of carbon dioxide at the point of contact with the substrate;

FIGURE 3 is a cross-sectional elevational view of an embodiment of the present invention which permits cleaning of a wide area in comparison with the embodiments shown in Figures 1 and 2;

FIGURE 4 is a top elevational view of the embodiment shawn in Figure 3.
FIGURE 5 is a cross-sectional elevational view of an embodiment of the passent invention which may be utilized for cleaning the inside surface of cylindrical structures.

in the drawings, like reference numerals indicate like parts.

Referring to the drawings, and specifically to Figure 1, the apparatus 2 of the present invention includes a fluid carbon dioxide receiving port 4 which is connected to a fluid carbon dioxide storage facility (not shown) via connecting means 6. The connecting means 6 may be a steel reinforced letten hose of any other suitable. connecting means which enables the fluid carbon dioxide to flow from the sources to the receiving port 4.

There is also provided a chamber 8 which receives the fluid carbon dioxide as fifthers through the receiving port 4. The chamber is connected via a first ortifice 10 to a nozzle 12. The nozzle 12 includes a coalescing chamber 14, a second orifice 16, and an election spout 18 terminating at an exit port 20.

The first orifice 10 includes walls 22 which taper toward an opening 24 into the coalescing chamber 14. The first orffice 10 is dimensioned to deliver about 0.25 to 0.75 standard cubic foot per mitute of carbon dioxide. The width of the first orifice 10 is sultably 0.050 to 0.050 inch and tapers slightly (ag about 1°), thus further accelerating the flow of the fluid carbon dioxide and contributing to the pressure drop resulting in the formation of the fine liquid droplets in the coalescing chamber 14.

In one embodiment of the Invention as shown in Figure 1, the first ordice 10 may be equipped with a standard needle valve 26 having a tapered snout 28 which is movable within the that ordice 10 to control the cross-sectional area thereof and thereby control the flow of the fluid carbon gloxide in an alternative embodiment, the first orifice 10 may be used alone without a needle valve. In this event, the width or diameter. of the orifice 10 is suitably from about 0.001 to about 0.050 inch. The needle valve 26 is preferred however. because it provides control of the cross-sectional area of the first office it the needle valve 26 may be

manipulated by methods customarily employed in the art, such as by the use of remote electronic sensor.

The cealescing chamber 14 comprises a rearward section 30 adjacent the first or lace 10 and communicating therewith via the opening 24. The coalescing chamber 14 also includes a forward section 34 The length of the coalescing chamber is sultably from about 0.125 to 2.0 inches, and the diameter is sultably from about 0.03 to 0.125 inch. However, it should be understood that the dimensions can vary according to the size of the job, for example, the size of the object to be cleaned. Although a coalesoling chamber 14 having a larger diameter will provide denser particles and therefore greater diaming intensity, it has been found that too large a diameter may result in freezing of moisture on the substrate surface which inhibits cleaning. This problem can be alleviated by lowering the ambient humidity. On the other hand, cleaning applications involving very delicate substrate surfaces may benefit from employing a small diameter coelecting chamber, 14

The diameter of the first orffice 10 can vary at well. However, if the diameter is too small, it becomes difficult to manufacture by the usual technique of drilling into bar stock. In general, the cross-sectional areas of the first ortfice 10 and second ortfice 16 are less than the cross-sectional area of the coalescing chamber 14

The source of carbon dioxide utilized in this invention is a fluid source which is stored at a temperature and pressure above what is known as the "triple point" which is that point where either a muid or a cas will turn to a solid upon removal of heat. It will be appreciated that unless the fluid carbon dioxide is above the triple point, it will not pass the orifices of the apparatus of this invention.

The source of carbon dioxide comtemplated herein as in a liquid state, is liquid, gaseous or a mixture thereof, at a pressure of at least the freezing point pressure, or about 65 psla and, preferably, at least about 300 psla.

The fluid carbon dioxide must be under sufficient pressure to control the flow through the first criffice 10 Typically, the fluid carbon dioxide is stored at ambient temperature at a pressure of from about 300 to 1000 psia, preferably at about 750 psia. It is necessary that the nthalpy of the fluid carbon dioxide feed stream under the above pressures be below about 135 BTU per pound, based on an enthalpy of zero at 150 pela for a satuarated liquid. The enthalpy requirement is essential regardless of whether the fluid carbon dioxide is in a liquid, gaseous or, more commonly, a mixture, which typically is predominately liquid. If the subject apparatus

is formed of a suitable metal, such as steel or tungsten carbide, the enthalpy of the stored fluid carbon dioxide can be from about 20 to 135 BTU/lb. In the event the subject apparatus is constructed of a resinous material such as, for example, high-impact polypropylene, we have found that the enthalpy can be from about 110 to 135 BTU/lb. These values hold true regardless of the ratio of liquid and gas in the fluid carbon dioxide source.

In operation, the fluid carbon dioxide exits the storage tank and proceeds through the connecting means 6 to the receiving port 4 where it then enters the storage chamber 8. The fluid carbon dioxide then flows through the first orifice 10, the size of which may, optionally, be regulated by the presence of the needle valve 26.

As the fluid carbon dioxide flows through the first orifice 10 and out the opening 24, it expands along a constant enthalpy line to about 80-100 psia as it enters the rearward section 30 of the coalescing chamber 14. As a result, a portion of the fluid carbon dioxide is converted to fine droplets. It will be appreciated that the state of the fluid carbon dioxide feed will determine the degree of change that takes place in the first coalescing chamber 14, eg saturated gas or pure liquid carbon dioxide in the source container will undergo a proportionately greater change than liquid/gas mixtures. The equilibrium temperature in the rearward section 30 is typically about -57°F and, if the source is room temperature liquid carbon dioxide, the carbon dioxide in the rearward section 30 is formed into a mixture typically comprising about 50% of fine liquid droplets and about 50% carbon dioxide vapor. If the source is saturated gas at room temperature, then the mixture typically comprises about 11% fine liquid droplets and 89% vapor. Accordingly, a mixture can be formed with a composition between these two.

The fine liquid droplet/gas mixture continues to flow through the coalescing chamber 14 from the rearward section 30 to the forward section 34. As a result of additional exposure to the pressure drop in the coalescing chamber 14, the fine liquid droplets coalesce into larger liquid droplets. The larger liquid droplets/gas mixture forms into a solid/gas mixture as it proceeds through the second orifice 16 and out of the exit port 20 of the ejection spout 18.

Walls forming the ejection spout 18 and terminating at the exit port 20 are suitably tapered at an angle of divergence of about 4° to 8°, preferably about 6°. If the angle of divergence is too great (ie above about 15°), the intensity of the stream of solid/gas carbon dioxide will be reduced below that which is necessary to clean most substrates.

The coalescing chamber 14 serves to coalesce the fine liquid droplets created at the rearward section 30 thereof into larger liquid droplets in the forward section 34. The larger liquid droplets form minute, solid carbon dioxide particles as the carbon dioxide expands and exits toward the substrate at the exit port 20. In accordance with the present invention, the solid/gaseous carbon dioxide having the requisite enthalpy as described above, is subjected to desired pressure drops from the first orifice 10 through the coalescing chamber 14, the second orifice 16 and the ejection spout 18.

Although the present embodiment incorporates two stages of expansion, those skilled in the art will recognize that nozzles having three or more stages of expansion may also be used.

The apparatus of the present invention may, optionally, be equipped with a means for surrounding the solid carbon dioxide/gas mixture as it contacts the substrate with a nitrogen gas envelop to thereby minimise condensation of the substrate surface.

Referring to Figure 2, the apparatus previously described as shown in Figure 1 contains a nitrogen gas receiving port 40 which provides a pathway for the flow of nitrogen from a nitrogen source (not shown) to an annular channel 42 defined by walls 44. The annular channel 42 has an exit port 46 through which the nitrogen flows toward the substrate surrounding the solid/gas carbon dioxide mixture exiting at exit port 20. The nitrogen may be supplied to the annular channel 42 at a pressure sufficient to provide the user the needed sheath flow at ambient conditions.

Figures 3, 4 and 5 illustrate additional embodiments of the present invention. The structure shown in Figures 3 and 4 has a flat configuration and produces a flat spray ideal for cleaning flat surfaces in a single pass. This configuration is particularly suitable for surface cleaning silicon wafers during processing when conventional cleaning techniques utilized on unprocessed wafers cannot be used due to potential harmful effects on the structures being deposited on the wafer surface. The designations in Figures 3, 4 and 5 are the same as utilized in Figures 1 and 2.

In Figure 3, the flat spray embodiment is illustrated in cross-sectional view, and the same device is shown in top view in Figure 4. Fluid carbon dioxide from the storage tank (not shown) enters the apparatus via the connecting means 6 through the first orifice 10. The coalescing chamber consists of a rear portion 30 and a forward portion 34 which make up the coalescing chamber 14. A single coalescing chamber 14 having the same width as the exit port 20 will be adequate. However, the pressure of the device requires that there be mechanical support across the width of the coalescing chamber 14. Accordingly, a number of mechanical supports 48 are spaced across the coalescing chamber 14 as shown in Figure 4. The number of channels formed in the coalescing chamber 14 is solely dependent on thenumber of supports 48 required to stabilize an exit port 20 of a given width. It will be appreciated that the number and size of the resulting channels must be such as to not adversely effect the consistency and quality of the carbon dioxide being supplied to the inlet of the second orifice 16.

The larger liquid droplets/gas mixture which forms in the forward section 34 of the coalescing chambers forms into a solid/gas mixture as it proceeds through the secondorifice 16 and out of the exit port 20, both of which have elongated openings to produce a flat, wide spray. The height of the openings in the second orifice 16 is suitably from about 0.001 to about 0.005 inch. Although the height of the opening can be less, 0.001 inch

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Is a practical limit since it is difficult to maintain a uniform elongated opening substantially less than 0.001 inch in height. Conversely, the height of the second orffice 16 can be made greater than 0.005 inch which does produce intense cleaning. However, at heights above 0.005 inch, the amount of carbon dioxide required to improve cleaning increases substantially. These dimensions are given as illustrative since there is no fundamental limit to either the width of the height of the second orifice 16. The appearatus shown in Figures 3 and 4 has been demonstrated to produce excellent cleaning of flat surfaces, such as silicon waters.

The embodiment of the present invention shown in Figure 5 is intended for cleaning of the inside of cylindrical structures. It is typically mounted on the end of a long tribular connector means 6 through which fluid carbon dioxide is transported from a storage means (not shown). In operation, the device shown in Figure 5 is inserted into the cylindrical structure to be cleaned, the fluid carbon dioxide turned on, and the device slowly withdrawn from the structure sweeps the interior surface of the cylindrical structure and the vaporized carbon dioxide carries released surface particles along as it exits the tube in from of the advancing jet.

In the embodiment shown in Figure 5, fluid carbon dioxide from a source not shown enters the device through connecting means 6. The fluid carbon dioxide enters the apparatus through the entry port 4 into a chamber 8. The chamber 8 is connected via a first orifice 10 to a nozzle 12. The nozzle 12 includes port 50 which lead to a coalescing chamber 14 and an exit port 20. In the embodiment shown in Figure 5, the exit port 20 and the second orifice 16 are combined.

In the apparatus shown in Figure 5, there is no divergence of the combined second office/exit port 20 since the orifice itself is divergent by nature due to its increasing area with increasing radius. The angle of incline of the second orifice/exit port 20 must be such that the carbon dioxide carons from surface to be cleaned with sufficient force to carry dislodged particles from the surface out of the attructure in advance of the umbrella-shaped jet. On the other hand, the angle cannot be too acute so as to deter from the cleaning capacity of the jet. In general, the second orifice/exit port 20 is inclined from the exis by about 30° to 90°, preferably about 45°, in the cleaning direction of the apparatus.

Commercially pure carbon dioxide may be acceptable for many applications, for example, in the field of optics, including the cleaning of telescope mirrors. For certain applications, however, "ultrapure" carbon dioxide (99.99% or higher) may be required, it being understood this purity is to be interpreted with respect to undestrable compounds for a particular application. For example, mercaptans may be on the list of impurities for a given application whereas nitrogen may be present. Applications that require ultrapure our on dioxide include the cleaning of silicon waters for semiconductor labification, disc drives, hybrid circuit assembles and compact discs.

For application requiring ultrapure carbon dioxide, it has been found that usual nozzle materials are unsatisfactory due to the generation of particulate contamination. Specifically, stabiless steel may generate particles of steel, and nickel coated brass may generate nickel. Po eliminate undestrable particle generation in the area of the orifices, the following materials are preferred: sapphire, fused silica, quartz, tungsten carbide, and poly(tetrafluoroethylene). The subject nozzles may consist entirely of these materials or that have a coating thereof.

The livention can effectively remove particles, hydrocarbon films, particles embedded in oil and finger prints. Applications include, but are not limited to the cleaning of optical appendix, space craft, semiconductor wafers, and equipment of contaminant-free manufacturing processes.

While the present invention has been particularly described in terms of specific emissionments thereof, it will be understood that numerous variations of the invention are within the skill in the air, which variations are yet with the instant teachings. Accordingly, the present invention is to be broadly construed and limited only by the scope and the spirit of the claims appended hereto.

### Example 1

Apparatus in accordance with the present invention was constructed as follows. A cylinder of Grade 4 Airco carbon dioxide equipped for a liquid withdrawal was connected the a six tool langth wire reinforced poly(tetrafluoroethylene) flexible fices to storage chamber 8 (see Figure 1). The lifts office 10 connecting the storage chamber 8 and the coalescing chamber 14 was fitted with a fine metal-lig valve 26 (Nupro S-SS-4A).

The nozzle 12 was constructed of 1/4 inch OD brees bar stock. The coalesotrip chamber 14 had a diameter of 1/16 inch measured two inches from the opening 24 to the second criftice 16 flaving a length of 0.2 inch and an internal diameter of 0.031 inch. The ejection spoul 18 was tapered at a 5° angle of divergence from the end of the second ordice 16 to the exit port 20 through a length of about 0.4 flaving.

Test surfaces were prepared using two inch diameter silicon waters purposely contaminated with a spray of powdered zinc containing material (Sylvania material #2284) suspended in ethyl alsohol. The waters were then sprayed with Freon from an aerosol container.

In preparing to clean the above-described substrate in accordance with the preparint invention, the Nuprovalve 28 was adjusted to give a carbon dioxide flow rate of approximately 178 SCFM. The nozzle 12 was operated for about five seconds to get the proper flow of carbon dioxide particles and then positioned about 1 1/2 inches from the substrate at about a 75° angle with respect to the substrate surface.

Cleaning was done by moving the nozzle manually from one side to the other side of thew water. The cleaning process was momentarily discontinued at the first sign of moisture condensing on the water surface.

Ultraviolet light was used to locate grossly contaminated areas that were missed in the initial cleaning run. These areas were thin cleaned as described above.

The resulting cleaned wafer was viewed under an electron microscope to automatically det ct selected particulates containing zinc. The results are shown in Table 1.

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## Table 1

10	Particle Size	% Particles Removed	
15	1.0 micron 0.1 to 1.0 micron	99.9 + % 99.5-%	· - -

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#### Claims

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1. Apparatus for removing small particles from a substrate comprising:

(a) a source of fluid carbon dioxide under pressure and having an enthalpy of below about 135 BTU per pound based on an enthalpy of zero of 150 psia for a saturated liquid, so that at solid fraction will form upon expansion of the fluid carbon dioxide to the ambient pressure of said substrate;

(b) a first expansion means (10) for expanding a portion of the fluid carbon dioxide obtained from the source into a first mixture containing gaseous carbon dioxide and fine droplets of liquid carbon dioxide;

(c) a coalescing means (14) operatively communicating with the first expansion means (10) for converting said first mixture into a second mixture containing gaseous carbon dioxide and larger liquid droplets of carbon dioxide;

(d) a second expansion means (16) operatively communicating with the coalescing means (14) for converting said mixture into a third mixture containing solid particles of carbon dioxide and gaseous carbon dioxide;

(e) means (20) communicating with said second expansion means for directing said third mixture toward the substrate.

Apparatus according to Claim 1, further comprising means (44) for directing a stream of nitrogen gas toward said substrate, said stream surrounding said third mixture as the third mixture contacts the substrate.

3. Apparatus according to Claim 1 or Claim 2, further comprising means for controlling the rate of flow of fluid carbon dioxide into the first expansion means.

4. Apparatus according to any preceding claim, wherein the first expansion means (10) comprises a first orifice (10) having a first opening in communication with the source of fluid carbon dioxide and a second opening leading to said coalescing means (14), said coalescing means (14) comprising a coalescing chamber (14) having a rearward section (30) in communication with said second opening, said rearward section (30) having a cross-sectional area greater than the cross-sectional area of the first orifice (10) thereby to enable the fluid carbon dioxide flowing through the first orifice (10) to undergo a reduction of pressure as the fluid carbon dioxide enters the rearward section (30) of the coalescing chamber (14) thereby to form said first mixture.

5. Apparatus according to Claim 4, wherein the coalescing chamber (14) further comprises a forward section (34) adjacent said rearward section (30) and having an opening leading to a second orifice (16) wherein the first mixture undergoes coalescing of the fine drops into larger drops of liquid carbon dioxide as it passes from said rearward section (30) to said forward section (34) thereby to form said second mixture.

6. Apparatus according to Claim 5, wherein the second expansion means (16) comprises said second orifice (16) having an opening at one end leading to the forward section (34) of the coalescing chamber (14) and another end opening into said third mixture directing means (20), said second orifice (16) having a cross-sectional area less than the cross-sectional area of the forward section (34) of the coalescing chamber (14).

7. Apparatus according to Claim 6, wherein the means (20) for directing said third mixture comprises a divergently tapered channel (20) communicating at one end with the second orifice (10) and having an exit port through which, in use the third mixture exits and contacts the substrate.

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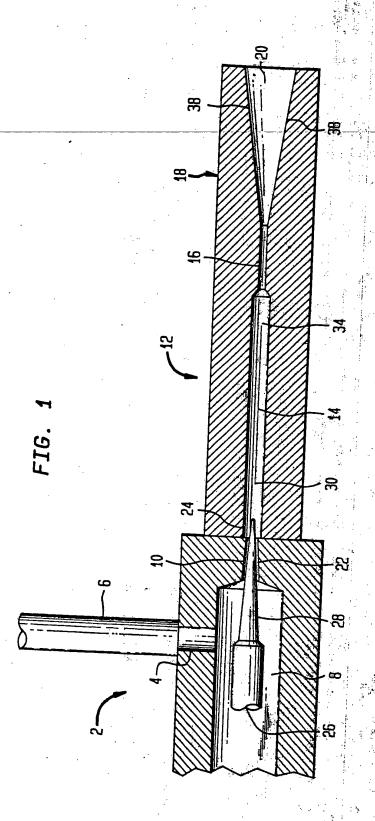
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- 8. Apparatus according to Claim 7, wherein te divergently tapered channel has an angle of divergence of up to 15°.
- 9. Apparatus according to any one of Claims 4 to 8, wherein the forward section of said coalescing means and said directing means have elongated opinings, thereby producing a wide flat spray.
- 10. Apparatus according to Claim 1 or 2, wherein the second expansion means (16) and the means (20) for directing the third mixture toward the substrate are combined in the form of a passag which communicates with a chamber (14) defining said coalescing means (14) and at its other end has an exit port through which in use the third mixture exits and contacts the substrate.
- 11. A method for removing particles from a substrate surface comprising:
  - (a) Converting fluid carbon dioxide into a first mixture of fine droplets of liquid carbon dioxide and gaseous carbon dioxide;
  - (b) converting said first mixture into a second mixture containing larger droplets of liquid carbon dloxide and gaseous carbon dloxide;
  - (c) converting said secnd mixture into a third mixture containing solid carbon dioxide particles and gaseous carbon dioxide; and
  - (d) directing said third mixture toward the substrate whereby said third mixture removes said particles from the substrate.
- 12. A method according to Claim 11, wherein said fluid carbon dioxide is liquid carbon dioxide.
- 13. A method according to Claim 11 or 12, further comprising storing the fluid carbon dioxide at a pressure of about 300 to 1000 psia.
- 14. A method according to any one of Claims 11 to 13, wherein step (a) comprises expanding the fluid carbon dioxide along a constant enthalpy line to about 80 to 100 psia.
- 15. A method according to any one of Claims 11 to 14, wherein the first mixture comprises from 11 to 50% of fine liquid droplets and from 89 to 50% of carbon dloxide vapor.



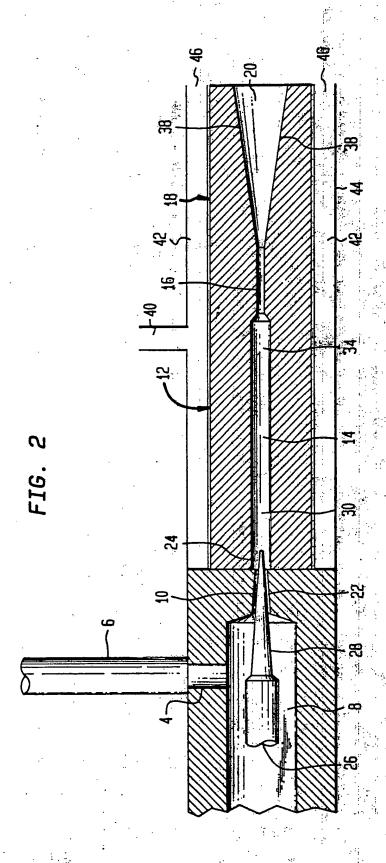


FIG. 3

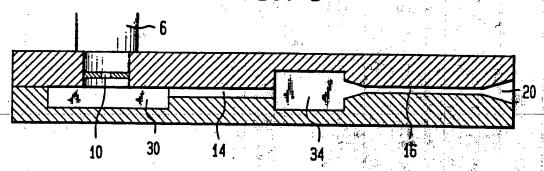
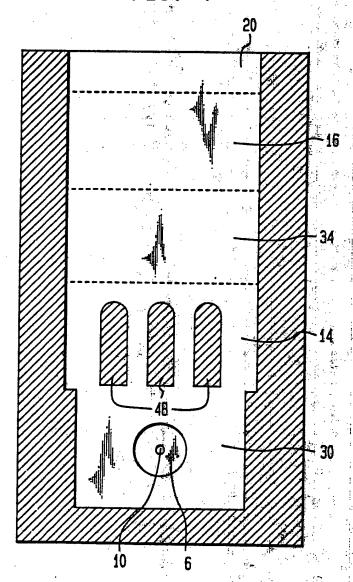
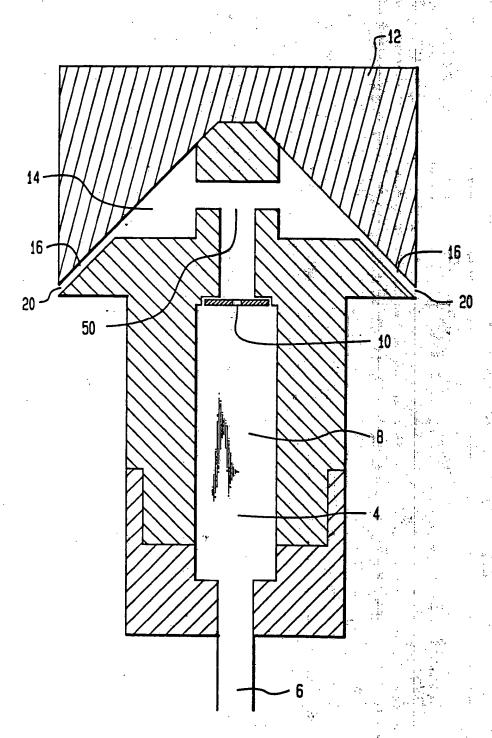


FIG. 4







(f) Publication number:

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## **EUROPEAN PATENT APPLICATION**

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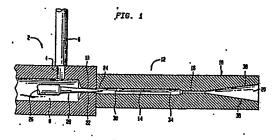
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Apparatus and method for removing minute particles from a substrate.

Apparatus for removing small particles from a substrate comprises a source of fluid carbon dioxide, a first orifice (10) for expanding a portion of the fluid carbon dioxide and find droplets of liquid carbon dioxide, a coalescing chamber (14) for converting the first mixture into a second mixture containing gaseous carbon dioxide and larger liquid droplets of carbon dioxide, a second expansion orifice (16) for converting said second mixture into a third mixture containing solid particles of carbon dioxide and gaseous carbon dioxide, and a divergent channel 20 having an exit port arranged to direct mixture toward the substrate. In using the apparatus, a source of fluid carbon dioxide having an enthalpy below about 135 BTU per pound (based on an enthalpy of zero at 150 psia for a saturated liquid) is employed.





# EUROPEAN SEARCH REPORT

EP 88 30 3551

	DOCUMENTO CO.			EP 88 30 3	55.
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Y,D	HOENIG: "Cleaning	AGAZINE, August 1986, Hipsburg, US; S.A. J surfaces with dry	1,2,4-8,10-12	H 01 L 21/00 B 08 B 3/02 B 24 C 1/00 C 01 B 31/22	
Y	CH-A- 134 733 ( OCTROOIMAATSCHAPP * Whole document	MIDDEN-EUROPEESCHE !J) *	1,2,4-8 ,10-12		
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	The present search report has	been drawn up for all claims			
Place of search		Date of completion of the search	<del></del>	Examiner	
THE HAGUE  CATEGORY OF CITED DOCUMENTS  X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		11-07-1989	VOLLER	VOLLERING J.P.G.	
		territory of print  E: earlier patent after the filing  D: document cite  L: document cite	T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons  &: member of the same patent family, corresponding		
P : inter	mediate document	& : member of the document	same patent family, co	rresponding	